INEEL/CON-99-01103
PREPRINT

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M. K. Harrup
A. K. Wertsching
F. F. Stewart

March 25, 2000 – March 29, 2000

American Chemical Society 219th National Meeting

BECHTEL BWXT IDAHO, LLC

Phosphazene Silicate Nanocomposites. A Survey of Materials Properties and Synthetic Methods Using New Catalysts.

Mason K. Harrup, Alan K. Wertsching, and Frederick F. Stewart*

Idaho National Engineering and Environmental Laboratory,
P. O. Box 1625, Idaho Falls, ID 83415-2208

Introduction

In the ceramics community, manipulation of synthetic conditions such as the choice of acid, base or ionic species as catalysts, aging of precursor solutions, and choice of sintering temperatures in the formation of silicate networks are known to produce radically different glass and ceramic morphologies.[1] Implementation of these approaches has been attempted for some organic polymer based hybrid nanocomposites[2] but not for polyphosphazene silicate composites. The desire to create unique and novel network morphologies became the impetus for establishing new catalysis protocols. The surprising inability to reproduce the mechanical properties of a well-established benchmark composite material from the literature,[3] was one principal driver that initiated this in-depth investigation into the roles that the nature and amount of catalysts play in the production and physical properties of these composites.

It quickly became apparent, in the course of experiments, that use of lower critical solubility temperature (LCST) purified methoxyethoxyethoxyphosphazene (MEEP)[4], instead of dialysis purified MEEP, prevented our attempts to successfully reproduce the mechanical properties reported for MEEP composites using the Ferrar method (for elaboration, see below).[3] Only after salt (as NaCl) was incorporated as a co-catalyst in the MEEP, did the Ferrar method produce tractable composites in our hands. This result suggests that in order for dilute acid (as HCl) to catalyze the silicate formation, an ionic salt co-catalyst was necessary. The opportunity to explore salt-only catalyzed composites became possible with the availability of rigorously pure MEEP. In addition, the ability to synthesize a series of acid or base catalyzed composites both with and without salt interference as a co-catalyst has provided us with the ability to decouple mixed catalyst effects on the properties of the composites.

Multiple series of composites were produced using a variety of synthetic conditions in an attempt to create and optimize desirable physical properties. The synthetic variables initially identified as critical and subsequently explored include the nature of the catalyst (acid, base or ionic salt), concentration of catalyst, and some mixed catalyst schemes. Other variables that are under current investigation include the effects of aging of the synthetic solution mixtures before casting, time of curing and the temperature at which the composites are cured. Composites, once formed, were subjected to mechanical and chemical analyses to evaluate and compare their properties. These materials have potential usefulness as solid electrolytes and also as durable membranes for separations applications in chemically aggressive environments.

Experimental

Synthesis of Composites. The general procedure given below is broadly applicable to the synthetic steps followed for the formation of all composites. A specific example for a base-catalyzed composite is as follows: MEEP (300 mg, 1.06 mmol) is dissolved into a 50/50 THF/ethanol (10 mL) mixed solvent in a capped vial. This solution is transferred into another vial containing TEOS (336 mg, 1.61 mmol). The KOH (0.50 M) catalyst is then introduced as an aqueous solution (150μL) and the mixture is capped and sonicated at 50 ^{o}C for 30 minutes. The solution was then aged for 2 hours in this sealed vial and poured into a Teflon mould and loosely covered at room temperature. The nanocomposite self-assembled as the volatile solvent slowly escaped during this curing process which lasted from between several hours to two days.

Mechanical Analysis. Each molecular composite was cast as a thin film and was cut to specific dimensions before analysis with TA Instruments Dynamic Mechanical Analyzer (DMA) equipped with a thin-film tension or penetration clamp accessory. Care was taken to ensure that these thin, elastic films were not overly stressed (beyond the linear region) during the removal from the casting moulds.

Results and Discussion

Catalysts such as lithium fluoride or potassium hydroxide have not previously been used in the formation of polyphosphazene silicate nanocomposites. Data collected from composites formed using these catalysts, with varying catalyst loading levels, are presented in Table 1. One notable trend in Table 1 is increasing composite strength with increasing concentration of LiF catalyst. Another is the relatively large displacement, above 6mm, for each LiF composite before failure. Large displacements are indicators of good aqueous swelling characteristics for these types of composites. All the LiF composites exhibit reproducible swell/deswell characteristics without damage to the structure of the ceramic component of the composite. Unfortunately this occurs with the loss of minor amounts of MEEP from the ceramic superstructure after repeated trials.

Although a correlation between strength and catalyst concentration for KOH composites is more ambiguous, the general trend is similar to that observed LiF composites. One advantage the KOH composites display is the large displacements, above 9 mm, in ramp force experiments. As expected from the data gathered on the LiF composites, KOH composites have excellent swell/deswell characteristics. Another advantage of the KOH catalyzed composites is that MEEP does not appear to leak out of the ceramic superstructure upon repeated swelling. This suggests a more intimately woven silicate polyphosphazene matrix as compared to composites catalyzed by LiF.

Table 1. Thin film force ramp (tension) study of MEEP/TEOS composites with variable aqueous (150 μL) catalyst concentrations.

Catalyst loading (M)	Max. Force (N) before failure	Displacement (μm)	Thickness (μm)
LiF 0.016	0.0583	6248.9	90
LiF 0.033	0.0961	7513	80
LiF 0.050	0.1457	6962.6	130
LiF 0.067	0.5764	6685.9	130
LiF 0.080	0.6523	11683	115
KOH 0.330	0.3545	9727	120
KOH 0.500	0.5146	10610	85
KOH 0.670	0.4265	10929	100
KOH 0.800	0.8064	17012	105

Whereas LiF and KOH composites typically form rubbery and highly adhesive materials, HCl/NaCl composites are less ductile, more glassy composites. High concentrations of halides in sol-gel cures are known by ceramists to encourage heavy cross-linking, which may explain this radical difference in morphologies. Stress-strain curves observed for these materials are very similar to those reported for the Ferrar composites.[3] This observation leads us to believe that the authors' were unaware of salt contamination in their source of MEEP. Both composites have short displacements before failure and similar maximum force limits (see Table 2). As the small displacements would indicate swelling in aqueous solution is poor and under hydrostatic pressure these composites fracture and fragment. Loss of MEEP from the composite occurs readily as the silicate matrix breaks up. An interesting caveat here is that increased cross-linking does not appear to significantly improve maximum force limits, as compared to the other composites.

Table 2. Acid with variable salt loading as a co-catalyst. Salt study of MEEP/TEOS solutions with 150 μL of 0.15 M HCl with various volumes of saturated aqueous NaCl co-catalyst.

sat. NaCl (μL)	Max. Force (N) before failure	Displacement (μm)	Thickness (μm)
0.0	NA (intractable)	NA	NA
10	0.6285	322	100
20	0.6180	985	60
30	0.9562	1041	120

The force ramp (tension) experiment was the initial analytical experiment performed on these composite films to gauge relative strengths. A representative plot is seen in Figure 1. The linear region as annotated is the

force range in which a material can be deformed in a fully reversible manner, that is the material retains full memory. For separations membrane applications, the linear region and displacement values are particularly useful data for assessing behaviour in aqueous feedstreams. In MEEP/silicate composites, the MEEP component is fully soluble in aqueous solutions while the silicate component is not. Force ramp displacements correlate well with dimensional changes that occur in the composites after swelling in water, and indicate whether or not internal hydrostatic pressure exceeds the linear force region of the composite. From this, the useful lifetime of the composite in actual water passing membrane applications can be estimated.

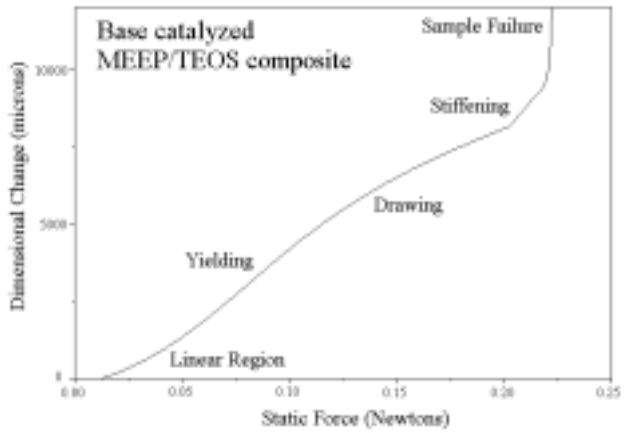

Figure 1. Typical data obtained from DMA force ramp experiments with base catalyzed molecular composites. Important features are labeled on the graphs.

For solid electrolyte applications, adhesion is a desirable physical property. However, it is critical to remain within the linear range (refer to Figure 1 above) when removing films from casting moulds. This can be particularly difficult when these composite films exhibit a high degree of adhesiveness. It was revealed through compression and penetration tests that highly adhesive thin films could be damaged if improperly peeled from

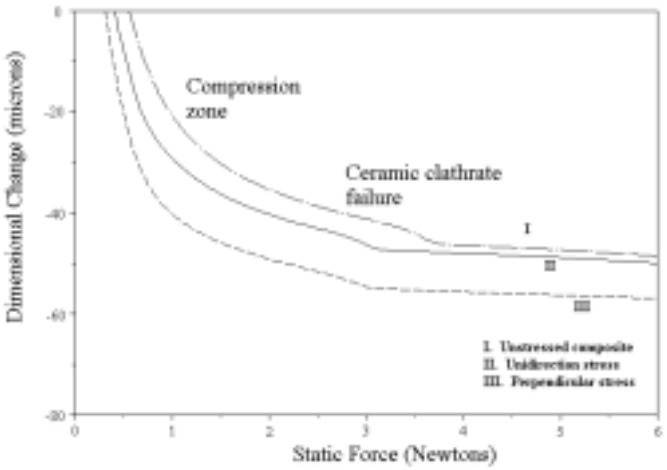

Figure 2. Compression (penetration) graph of KOH catalyzed MEEP/TEOS composite before (I) and after (II and III) an externally applied force.

casting moulds. The three force curves shown in Figure 2 are of a single composite sample exposed to increasing levels of stretching force applied by peeling the composite from a steel surface. The bottom curve is a composite stressed in two perpendicular directions, the middle curve is stressed in only one direction, and the top curve represents an unstressed sample. The point at which the silicate clathrate fails, as annotated, not only provides the force limit under compression, but the minimum composite thickness before failure while under compression. These compression force values indicate the level of stretching force to which a sample has been exposed. This method provides a facile method to evaluate data on composite experimental protocols such as casting and handling techniques.

Conclusions

Phosphazene silicate nanocomposites were synthesized and their mechanical properties analyzed. Three distinct types of catalysts were employed; acid, base and ionic salt species; resulting in a wide variety of mechanical properties. A survey of the effects of the nature of the catalyst and the amount of catalyst employed was conducted providing insight into synthetic strategies needed to produce composites with specifically tailored properties for a variety of applications.

Acknowledgement. The work described in this paper was supported by the United States Department of Energy through Contract DE-AC07-99ID13727 and the INEEL Environmental Science Research program.

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